

NGR-44-005-093
NGR-44-005-020
(In Press)

J. Gas Chromatog

GAS CHROMATOGRAPH-QUADRUPOLE MASS SPECTROMETRIC
ANALYSIS OF ORGANIC COMPOUNDS

W. S. Updegrave, J. Oro', and A. Zlatkis

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

Chemistry Department
University of Houston, Houston, Texas

FACILITY FORM 602
N67 18099
(ACCESSION NUMBER)
15
(PAGES)
CR 81 760
(NASA CR OR TMX OR AD NUMBER)

(THRU)
1
(CODE)
06
(CATEGORY)

ABSTRACT

An analytical gas chromatograph-mass spectrometer system was designed and built using standard simple subsystems, including a small quadrupole mass filter, to analyze mixtures of organic substances. Chromatographic and mass spectral data on the analysis of a sample consisting of acetonitrile, furan and pyrrole are presented. Other samples of aromatic hydrocarbons, paraffins and organic compounds of biological significance were also analyzed. Mass spectra of individual components in samples of a few micrograms were obtained without the use of molecular separators. The new apparatus yielded results which were equivalent but not identical to that obtained from an LKB 9000 instrument which was used as a standard for comparison. The data obtained with compounds of mass below 150 are reliable and promising results were also obtained with compounds of mass up to 500.

INTRODUCTION

The usefulness of sophisticated analytical gas chromatograph-mass spectrometer combinations currently in use has been well established. The integration of gas chromatography and mass spectrometry offers all the advantages inherent in either of these techniques with additional resulting advantages in the combination. These have been described and discussed in some detail mainly by Ryhage⁽¹⁾ Watson and Biemann⁽²⁾ Lipsky et. al.⁽³⁾ and Oro' et. al.⁽⁴⁾.

The present study demonstrates the analytical potential of an integrated instrument made of a standard general purpose gas chromatograph and a compact relatively simple low cost quadrupole mass analyzer.

EXPERIMENTAL

The experimental work consisted of building and testing a gas chromatograph-mass spectrometer combination of standard, but otherwise unrelated, sub-systems. A block diagram of this system is shown in Figure 1.

The gas chromatograph was a temperature programmed Barber-Colman system equipped with a stainless steel capillary column (1500 centimeters x 0.076 centimeters inside diameter) coated with 10 percent SF-96. The desired chromatographic separation was achieved through the proper choice of temperature and flow conditions. A stream splitter was constructed to direct approximately 80 percent of the effluent into the hydrogen flame detector and the remainder to the variable leak valve on the vacuum chamber. The connection between the chromatograph column splitter and the vacuum chamber was accomplished through the use of a stainless steel capillary (90 centimeters x 0.05 centimeters inside diameter) directed to the sapphire disc of the Varian bakeable variable leak valve. Adjustments of this valve permitted any choice of sample load to the mass spectrometer commensurate with the capabilities of the ion detector and

pumping system. A standard (60 centimeters x 30 centimeters inside diameter) bench top bell jar vacuum system was equipped with a 50 liter per second cold cathode sputter ion pump and a 4,000 liter per second hot filament titanium sublimation pump. Vacuum pressure measurements were made with the ion pump current. Within the vacuum system the sample was conveyed to the ionizer of the mass spectrometer through a pyrex tube (50 centimeters x 0.6 centimeters inside diameter), which was heated by vacuum-compatible General Electric Type T-3 quartz infrared heaters. A standard Ultek-EAI Quadrupole Model 250 Residual Gas Analyzer (Figure 2) was connected to the bell jar and served as an "analytical" mass spectrometer. Mass spectra achieved from this device were displayed on a Minneapolis-Honeywell 1508 Visicorder system.

The analytical procedure consisted of injecting 0.5 microliter of sample into the gas chromatograph under conditions of temperature and hydrogen carrier flow rates to produce peaks of approximately 30 seconds duration. The variable leak valve was adjusted to cause the pressure within the vacuum chamber to be less than 5×10^{-6} torr, but large enough to provide adequate sensitivity. Gas chromatograms and mass spectra were produced by the flame ionization detector and the quadrupole mass spectrometer, respectively. When the sample peak was registered on the strip chart recorder, *the corresponding* ^{*um*} ~~A~~ mass spectra ~~A~~ was displayed on the Visicorder by actuating the chart drive and sweep scan simultaneously. The peaks were scanned at a rate of approximately 4 seconds per 100 atomic mass units. The ion source conditions of the quadrupole-mass filter were established in keeping with the normal procedures set up as if using the instrument as a residual gas analyzer.

A tungsten filament was used to emit 70 electron volt electrons in the ion source.

RESULTS AND DISCUSSION

Typical results obtained with this system are illustrated in Figures 3 and 4. Figure 3 is a gas chromatogram of a sample made up of equal mole fractions of acetonitrile, furan and pyrrole. Figure 4 is the mass spectra of these three compounds obtained as each one emerged from the gas chromatograph.

The instrument was also applied to the analysis of mixtures of C_6-C_{10} normal paraffins and C_6-C_9 aromatic hydrocarbons. Perfluorokerosene and perfluorotributylamine were used for calibration purposes up to approximately 500 atomic mass units.

Practical sensitivities and adequate signal to noise ratios were achieved with sample sizes of 0.05 microliter and less. Scan speeds 5 milliseconds per atomic mass unit, or slower, give rise to well resolved mass spectra. Furthermore the data obtained with the integrated system indicates that the duration of the gas chromatographic peak should be approximately 10 times the mass scan time.

When using titanium sublimation pumping, and hydrogen carrier gas, a variable leak valve may be used to admit samples directly into the mass spectrometer ion source. Because of the high pumping rate for hydrogen and the wide dynamic range of this quadrupole mass analyzer, no means of gas enriching or molecular separation is necessary. Response times of the integrated system were such that no measurable peak broadening was produced by the mass analyzer. When operating the mass spectrometer at a resolution of approximately one part in 200, excellent data were obtained with samples up to 150 atomic mass units. It is expected that the performance of this device can be raised to permit the analysis of samples of molecular weight approaching 500 atomic mass units. At present, however, mass discrimination seems to limit the mass range. Mass spectra of certain biorganic substances produced by the quadrupole mass spectrometer are in general comparable, but not identical, to those obtained from the conventional laboratory analytical mass spectrometer system.

Current studies are being concentrated on the analytical determination of a) hydrocarbons and other molecules of presumed biological origin, e.g. phytane, pristane and farnesane; b) organic compounds resulting from the thermal outgassing of terrestrial and extraterrestrial samples; c) pyrolyzates of bacteria and other micro-organisms.

In summary, this work demonstrates that it is feasible to build a simple instrument for the mass spectrometric analysis of gas chromatographic effluents. It is hoped that continuation of this work will lead to the development of space flight instrumentation for the analysis of organic compounds, on planetary surfaces⁽⁴⁾.

ACKNOWLEDGEMENTS

We thank J. Miller, R. Wilkin, and R. Mathews for help in various phases of this work. These studies were supported in part by grants, NGR-44-005-043 and NGR-44-005-020, from the National Aeronautics and Space Administration.

LITERATURE CITED

1. Ryhage, R. Anal. Chem. 36, 759 (1964).
2. Watson, J. T., and Biemann, K. Anal. Chem. 36, 1135 (1964).
3. Lipsky, S. R., Horvath, C. G. and McMurray, W. J. Anal. Chem. 38, 1585 (1966).
4. Oro, J., Biemann, K., Gohlke, R.S., Lipsky, S.R., Lovelock, J.E., McLafferty, F.W., Meinschein, W. G., and Ryhage, R. in chapter "Analytical Methods for Landers", Rea, D.G. ed., in "Biology and the Exploration of Mars", Pittendrigh, C.S., Vishniac, W., and Pearman, J.P.T., eds., pp. 378-384, National Academy of Sciences National Research Council, Washington, D.C., 1966.

Figure 1

Block diagram of the gas chromatograph-
quadrupole mass spectrometer system.

BLOCK DIAGRAM G.C./ QUADRUPOLE M.S.

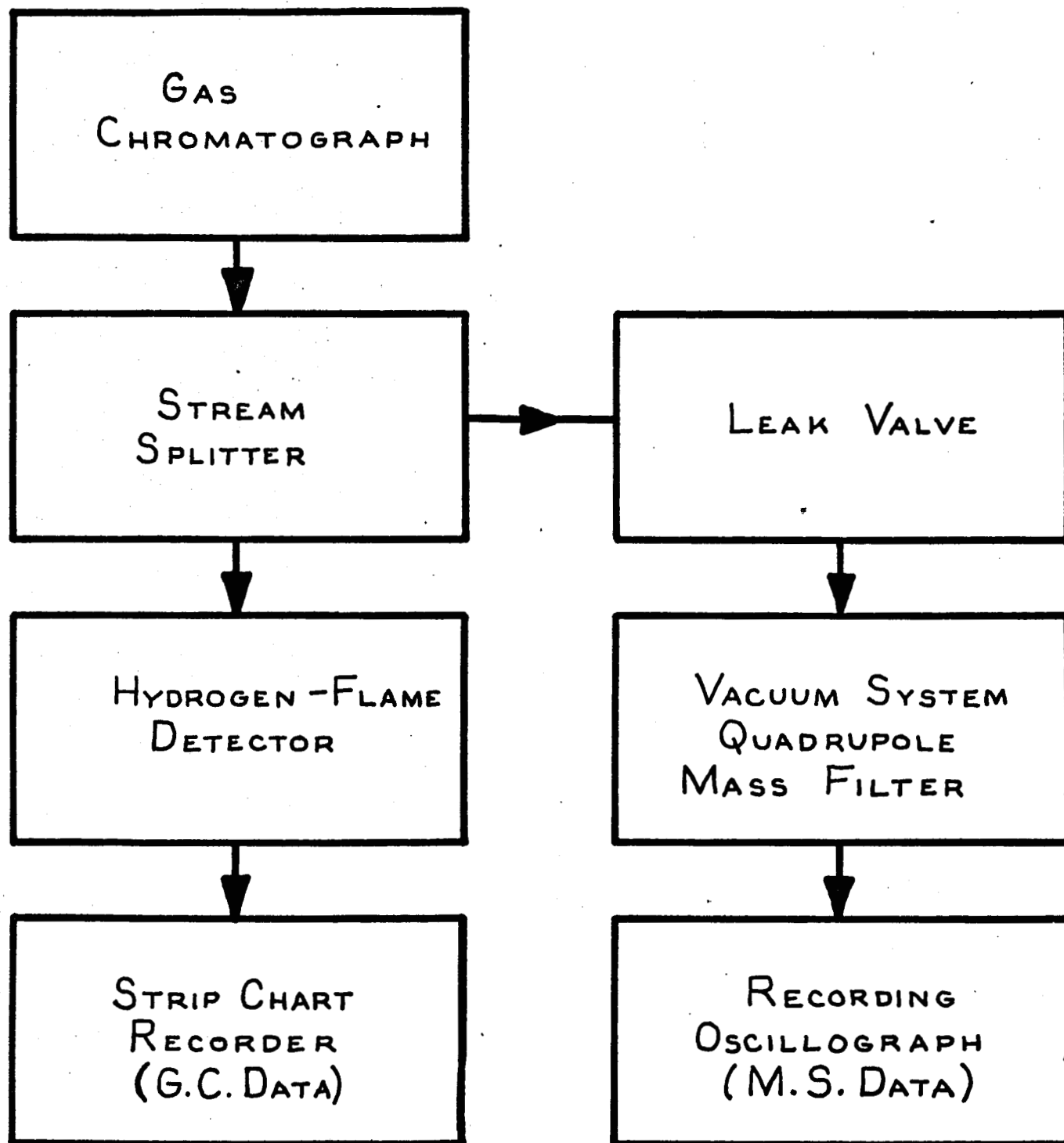
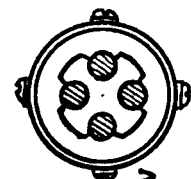
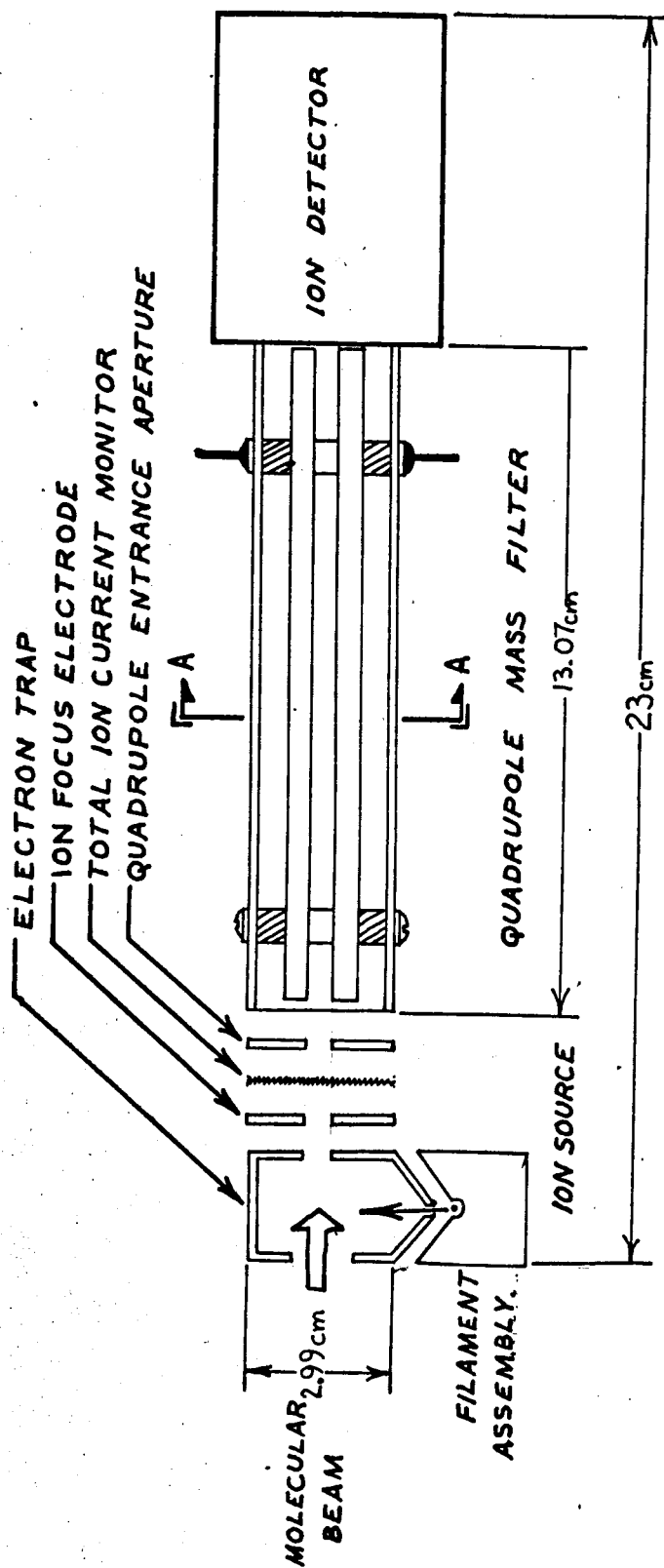


FIG. 1.

Figure 2

**Schematic diagram of the quadrupole
mass analyzer.**

QUADRUPOLE M.S.



MASS FILTER
CROSS-SECTION
A-A

Figure 3

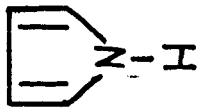
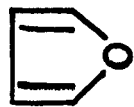
Gas chromatogram of a mixture of
acetonitrile, furan and pyrrole.

Column: 150 m x 0.76 mm inside
diameter. Substrate: 10% SF-96

(100). Temperature: 25°C.

Pressure: 10 psi H₂.

CH₃CN



5

10

15

20

25

30

35

40

45

50

TIME IN MINUTES →

Figure 4

Mass spectra of the compounds separated by gas chromatography (Figure 3) obtained with the quadrupole mass spectrometer. Total pressure 2×10^{-6} torr; tungsten filament, 70 eV electrons.

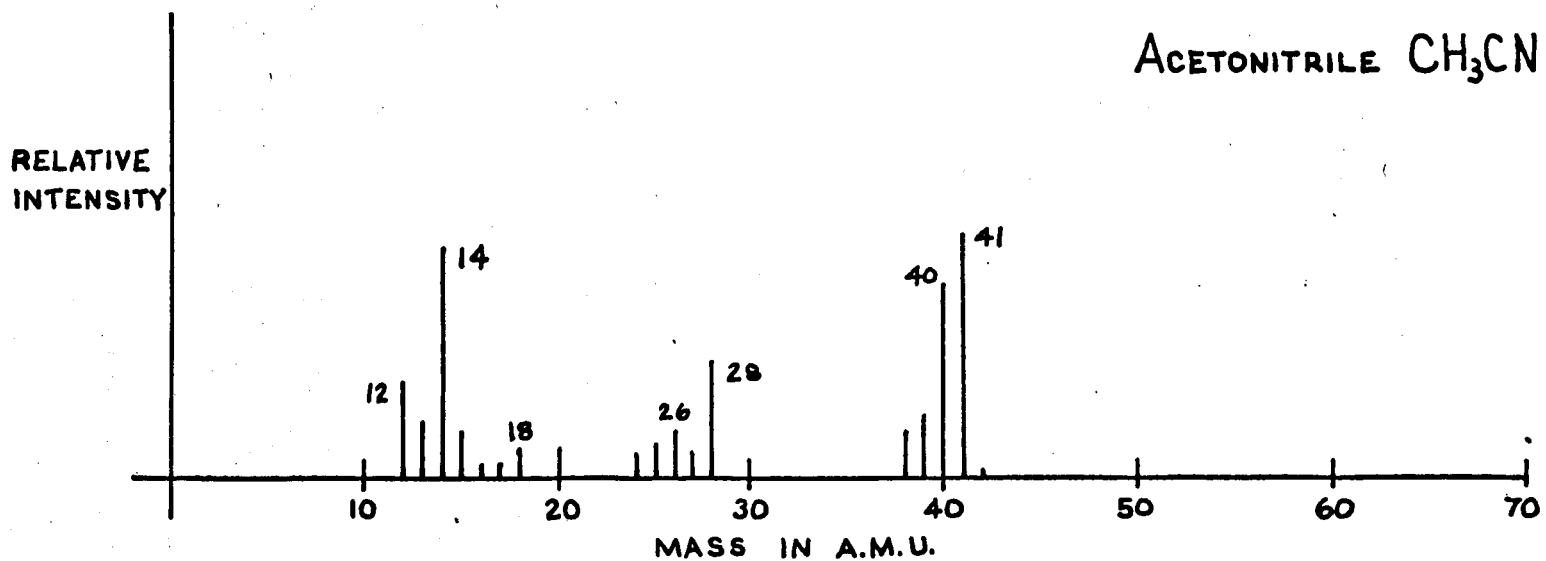
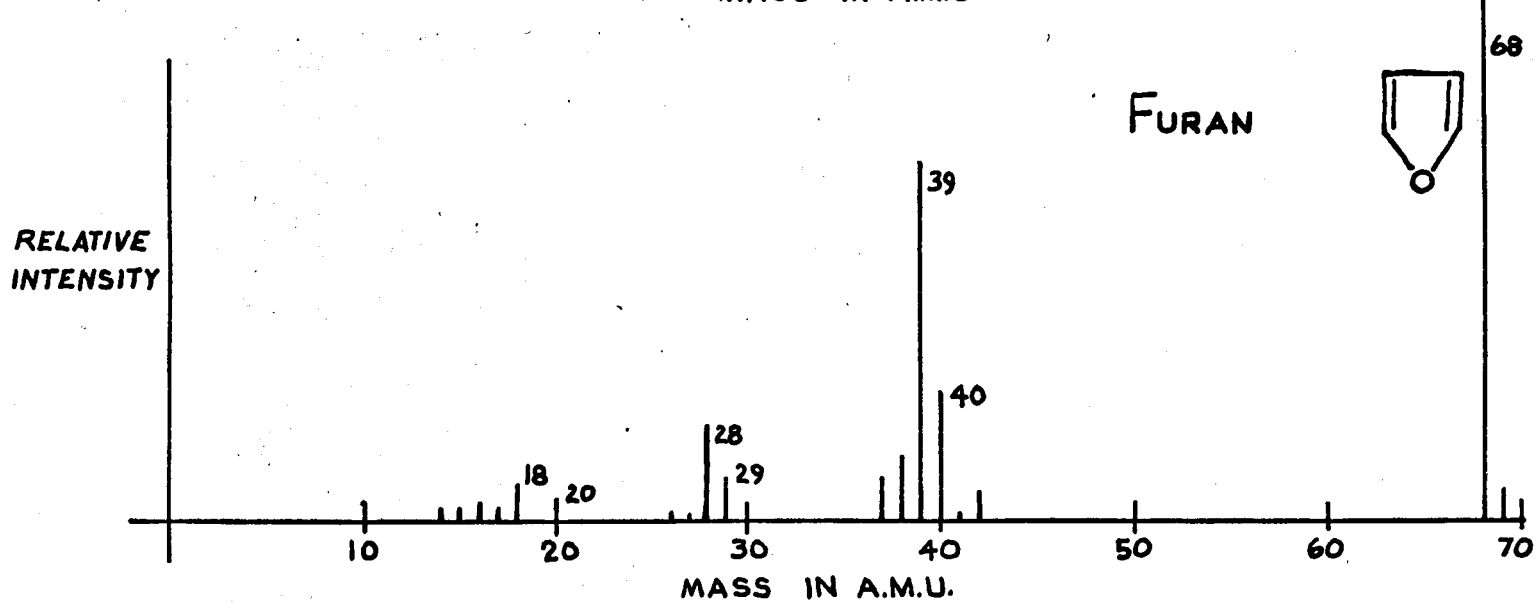
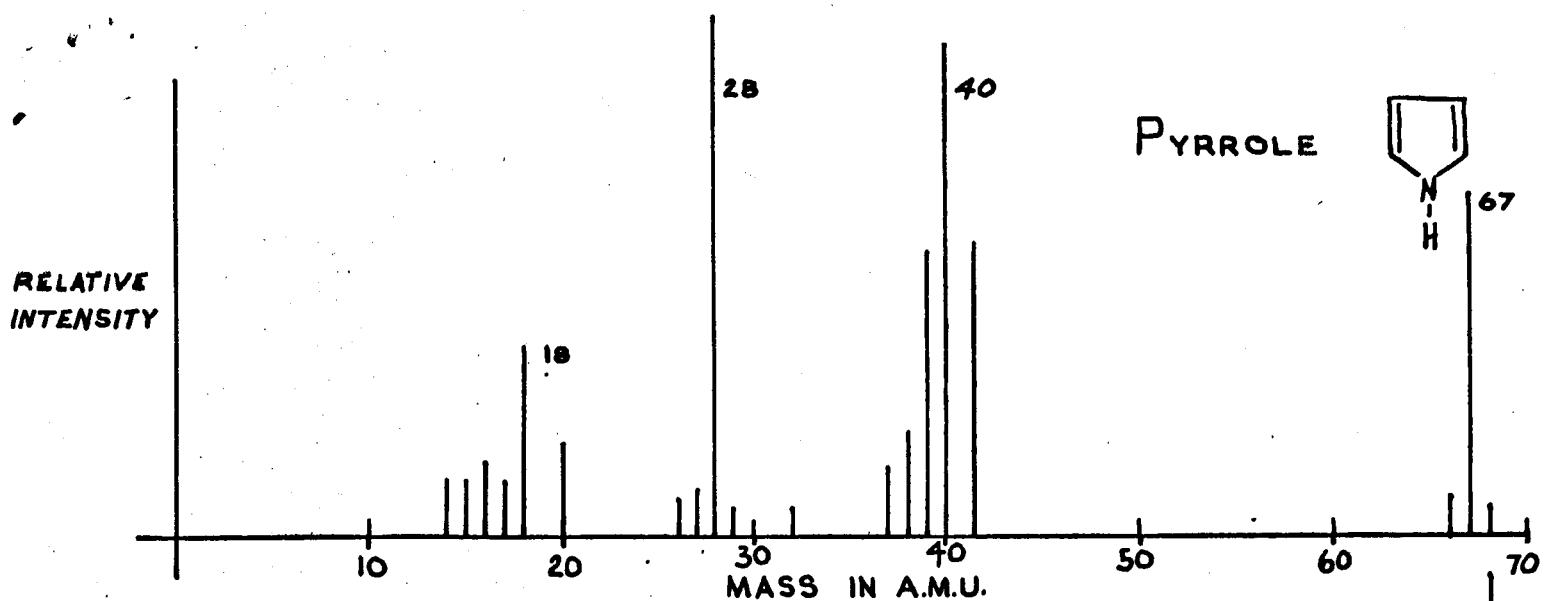


FIG. 4